STANFORD UNIVERSITY LIBRARY
APR 1 1927

A STUDY OF BREDIG GOLD SOLS

DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University

STANFORD UNIVERSITY LIBRARIES
WITHDRAWN

BY
JOHN PAGE AMSDEN, A.B., M.A.
NEW YORK CITY

1926

3781
C72A
UNCLASSED

TO MY

MOTHER AND FATHER

ACKNOWLEDGMENT

The author wishes to express his gratitude to Professor H. T. Beans, at whose suggestion this problem was undertaken, for his valuable advice, generous assistance, and friendly encouragement throughout its prosecution.

He is also indebted to Dr. Shear and to other members of the Chemistry Department for their co-operation.

A STUDY
OF
BREDIG GOLD SOLS

DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University

BY
JOHN PAGE AMSDEN, A.B., M.A.
NEW YORK CITY
1926

A STUDY OF BREDIG GOLD SOLS

I. Introduction

The composition of metallic hydrosols formed by the Bredig method of electrical dispersion[1] has been the subject of much speculation ever since the discovery of the method. Various theories have been advanced to explain both the formation of the particles and their growth in the sol. A large amount of work on chemically prepared hydrosols of the ferric oxide type has led to the general conclusion that the presence of minute amounts of electrolyte are essential to the formation of sols of this type,[2] the electrolyte forming some kind of complex with the dispersed phase.[3]

This "complex theory" for the structure of colloidal particles was not, however, extended to sols of the Bredig type. Gold sols of this type were thought to consist of a mechanical suspension of gold particles in water which did not settle out simply because they were too small.[4e] This explanation was adhered to in spite of the fact that Bredig himself,[1] and numerous others[4] since, have recommended the use of low concentrations of NaOH or HCl. It was still maintained that the presence of these electrolytes merely facilitated the formation of the sol. They were not essential and the sols could be prepared in pure water.[4]

In 1915 Beans and Eastlack[5] showed conclusively that Bredig gold sols cannot be prepared in water having a conductivity of 1×10^{-6} mhos. They showed that the presence of an electrolyte in concentrations ranging from .00005 M to .005 M is essential to the formation of a sol, and only those electrolytes which furnish an anion capable of combining chemically with gold can serve to stabilize these gold sols.

Since that time much work has been done in this laboratory on the part played by the electrolyte. These researches studied the amount of gold in a sol as related to the length of time that the arc was run in making the sol,[8] and also to the original concentration of electrolyte in the solution in which the sol was made.[7] They also studied the effect of different electrolytes on the character of the sol;[6,7] and the stability of the sol, or its ability to resist precipitation by centrifuging for varying times at varying

speeds.[8,9] The results all served to establish more firmly the original statements of Beans and Eastlack.

The first quantitative work on the composition of Bredig gold sols was done by Shear[10] in this laboratory. By means of potential measurements he was able to determine the concentration of electrolyte in the sol. He also determined the amount of colloidal gold present and was thus able to demonstrate that there is a relationship between the amount of electrolyte disappearing due to the formation of the colloidal complex and the amount of gold present in the sol. He proved definitely the existence of a complex, toward which conclusion all the previous work in this laboratory had pointed.

Shear and the author, as stated in Shear's thesis, showed that during the formation of gold sols with the direct current arc a considerable amount of electrolyte was lost due to electrolysis, there being present in the sol oxidation products of chloride ion. While this complication does not affect the validity of Shear's statement that a complex is formed, it does render inaccurate his determinations of the relationship between the loss of chloride ion activity due to the formation of the sol and the amount of gold present in the colloidal form. He attempted to correct his measurements by determining the fraction of the total loss of chloride ion activity which was due to electrolysis. In brief this was done by running a "blank", i.e., by electrolyzing some of the original solution under conditions as nearly as possible duplicating those under which the sol was made, and determining the amount of electrolyte lost due to this electrolysis alone.

This correction was of necessity inaccurate for the following reasons. The rate of electrolysis is not constant but is a function of the concentration of electrolyte present at any given moment. Therefore, since in the formation of the sol electrolyte is being lost not only because of electrolysis but also because of the formation of a complex, it is obvious that the results obtained from the "blank" are not applicable to the sol. Further, the products formed by electrolysis tend to react with water to re-form some chloride ion until equilibrium is reached. This reaction is comparatively slow and may account for the fact that some of Shear's sols showed an increase in chloride ion content upon standing. There is also the possibility, not yet proven, that the products of electrolysis themselves may be capable of stabilizing the sol.

Since the previous work on Bredig gold sols done in this laboratory used the direct current arc, the same objections apply more or less to the results obtained.

It was with the hope of eliminating electrolysis and its attendant complications, and thus gaining more precise information concerning Bredig gold sols, that the present work was undertaken.

II. Materials and Apparatus

The KCl used was C. P. KCl re-crystallized twice from conductivity water, dried and fused in a platinum dish, pulverized in an agate mortar, and kept in a dessicator. All solutions were made up in doubly distilled water having a specific conductivity of 0.9 to 1.2 x 10^{-6} mhos immediately before using. The solutions were made by dissolving the required amount of KCl in three liters of water and were kept in non-sol bottles which had been cleaned, steamed, and dried. All beakers, cells and bottles used were of either Pyrex or non-sol glass. All glassware and the gold wires were well cleaned, steamed and dried before using. The conductivity and potential measurements were made in a water thermostat maintaining a temperature of 25°.00 ± 0.°02 C. The Beckmann thermometer used in the thermostat was compared with a thermometer certified by the U. S. Bureau of Standards. The weights, flasks, and pipettes used were all calibrated.

The measuring instruments used were a Leeds and Northrup Type K potentiometer, a Type R galvanometer, a Weston standard cell, a Leeds and Northrup conductivity set-up, and a modified Freas conductivity cell[5] having a cell constant of 9.5 x 10^{-3}. The conductivity set-up consisted of a Vreeland oscillator furnishing a frequency of 1000 cycles per second, a Kohlrausch slide wire bridge, resistance boxes, and a variable condenser for balancing the capacity of the conductivity cell.

The Weston standard cell was checked at frequent intervals against a standard Marion Eppley cell No. 8246 and was found to give a value of 1.0187 volts which remained constant. The centrifuge was the same as described by Briggs.[8] The arcing stand was the same as described by Eastlack with the addition of a motor stirrer. The circuit used consisted of the following: a slide wire resistance of 31 ohms placed in series with the spark

gap and with a 110 volt, 60 cycle, alternating current lighting circuit; and a 1 microfarad, Western Electric telephone condenser placed in parallel across the spark gap. This circuit gave a current of approximately 3.5 amperes when the spark gap was closed.

III. Cell and Electrodes

The cell and electrodes used in the potential measurements were the same as described by Shear, but the author has learned from experience that certain precautions are necessary in their preparation and use which may not be obvious to the uninitiated. Therefore it seems advisable to note them here. The method used in preparing the electrodes follows that of MacInnes and Beattie.[11]

The electrodes consisted of squares of 35 mesh platinum gauze 1.5 cms. on a side, which were welded onto platinum wires. They were coated with silver by making them the cathode in a solution of $KAg(CN)_2$ with a pure silver anode. They were silver plated in this solution with a current of 3 milliamperes per electrode for 24 hours. It was found that a heavier current produced a flaky, non-adherent deposit of silver.

Following this silver-plating the electrodes were allowed to stand for 24 hours in distilled water, rinsing them at frequent intervals. It is essential that this washing be thorough as apparently the smallest amount of cyanide is sufficient to render them useless.

The electrodes were then coated with AgCl by making them the anode in an approximately .05 M KCl solution with a platinum cathode and electrolyzing for 20 minutes with a current of 7 milliamperes per electrode. It was found that a heavier current produced a spongy, non-adherent deposit. All electrodes which gave good results were found to be distinctly purple in color. After washing with distilled water they are now ready to be used. When not in use the electrodes should be washed and allowed to stand in dilute KCl solution. They should never be allowed to remain in a sol or stand in the air for any length of time.

If proper attention is paid to these precautions, consistently good electrodes may be expected which will last for about six sets of readings. Those left undisturbed in the reference half-cell often lasted for weeks.

If it is desired to remove the AgCl coating the NH_4Cl treatment described by Shear proved satisfactory. If it is desired to remove the silver also, concentrated HNO_3 is more satisfactory than KCN.

Electrodes made of silver gauze instead of silver-plated platinum were tried as a base for the formation of AgCl but these proved unsatisfactory.

The precautions to be observed in the use of the cell are that all joints, both rubber and glass, shall be paraffined tightly as the smallest leak destroys all accuracy. Also all electrical connections should be clean, bright and dry.

In making potential measurements, if the two electrodes in the same half-cell showed a potential difference greater than 0.5 millivolt, or if the potential between two standard KCl solutions, as measured in the cell, differed from the calculated value by more than ± 0.5 millivolt the electrodes were not used. It was found possible to obtain potential readings with a precision of ± 1 millivolt.

In addition to all the above, too much emphasis cannot be laid on the necessity of checking the electrodes with standard KCl solutions immediately before measuring each sol. Otherwise the results obtained in the sol are valueless. These check readings are indicated in Tables I, II, and III.

IV. Preliminary Investigations

Since the purpose of this work was to obtain information concerning Bredig gold sols which were not complicated by the presence of oxidation products of the electrolyte used it was necessary to ascertain whether or not the proposed method of making the sols resulted in detectable amounts of the oxidation products of chloride ion.

It was decided to use the starch-iodide test to see whether any electrolysis had taken place, and to determine the delicacy of this test the following experiments were made: 100 cc. of .0016 M KCl were electrolyzed for one minute with a direct current of 110 volts and .07 amperes. The solution gave a strong positive test with starch-iodide, thus indicating that the reagent was sensitive to minute amounts of oxidation products. Other solutions were then electrolyzed under the same conditions and the change in potential due to electrolysis was measured. These solutions were

then tested with starch-iodide, an immediate blue color being considered a positive test. The results are given below.

Solution .001 M KCl	Change in potential	Starch-iodide test
a	0. mv.	—
b	0. mv.	—
c	1. mv.	+ good
d	5. mv.	+ strong

This indicates that the starch-iodide test will detect amounts of oxidation products less than those which affect the accuracy of the experimentally determined potential readings which are precise only to one millivolt.

The next step was to obtain a method of preparing the sols which would not result in the production of detectable amounts of chloride ion oxidation products. A direct current of voltage below the oxidation potential of chloride ion would satisfy, but it was impossible to obtain an arc under these conditions. It was also impossible to obtain a satisfactory arc with the 60 cycle alternating current. Finally it was found that the use of a condenser in parallel across the gap resulted in a vigorous spark which gave satisfactory sols. These sols all gave a negative test for chloride ion oxidation products with starch-iodide. This method therefore was used. All sols used from this point on in the research were tested with starch-iodide and all gave a negative test. This method of preparing Bredig gold sols is similar to one described by Svedberg.[12] Svedberg has done a large amount of work on the preparation of Bredig gold sols using various types of currents and circuits, but has not given proper attention to the initial purity of the dispersion medium in the case of Bredig gold hydrosols. He does not define the purity of the water used and disregards the effect of small concentrations of electrolyte on the Bredig sols, although in the production of gold sols by reduction he states[12] that the addition of a chloride decreases enormously the time required for the formation of the colloid.

V. Method of Procedure

The desired amount of KCl solution was pipetted out into a well steamed and dried Pyrex beaker. This beaker was then placed in an ice bath and covered with a celluloid shield through which were three holes permitting the insertion of thermometer, stirrer, and electrodes into the solution. The stirrer was run at

approximately 100 r.p.m. and the temperature was always kept below 25°C. The spark was maintained for varying lengths of time and in order to make the results comparable these "sparking times" were expressed in hours per liter, i.e., if 100 cc. were sparked for one hour the time is given as 10 hours per liter. Since we are concerned only with the relationship between chloride ion activity lost and colloidal gold present, these sparking times are only approximate. It was found that a spark could not be maintained if only the tips of the electrodes were opposed. Therefore the gold wires were so placed that they overlapped each other about 5 mm. If they were then placed in contact and slightly released, a vigorous spark was obtained. For the shorter sparking times 250 cc. of KCl solution were used, but for the longer times only 100 cc. were used in order to avoid tediously long sparking times.

After the formation of the sol, it was decanted into a non-sol bottle. The difference of potential between silver chloride electrodes in the sol and in .005 M KCl was measured in the manner described by Shear. The sol was then centrifuged for 15 minutes at 1200 times gravity* and 25 cc. of the upper portion in the centrifuge tube were pipetted off for gold analysis. The gold in this was precipitated by the addition of 3 or 4 drops of 12 M HCl. It was then filtered through a Gooch crucible, heated to constant weight on a quartz plate and weighed. The filtrate was tested with freshly prepared starch-iodide.

The volumes used for potential measurements and centrifuging were so chosen that 100 cc. of sol sufficed for a complete determination. When a greater volume was available, the remainder was used for further experimentation, as will be described later.

VI. Results

The first series of sols were made in .001 M KCl since previous work in this laboratory[7] had established that this was approximately the optimum concentration for the formation of sols with the direct current arc. All potential measurements were made against .005 M KCl in a cell of the following type:

$$\text{Ag–AgCl} \mid \text{.005 M KCl} \parallel \text{Sol} \mid \text{AgCl–Ag}$$

The results are given in Table I.

* This centrifuging was done to remove suspended matter not colloidal in nature.

The calculated potentials between two standard KCl solutions were obtained from that form of Nernst's equation which applies to concentration cells,[13] using activities in place of concentrations. The activities for chloride ion were obtained from Lewis and Randall's Thermodynamics.[14] Nernst's equation then becomes: $E = \frac{RT}{n} \ln \frac{a_1}{a_2}$ or for KCl at 25°C, $E = .059 \log_{10} \frac{a_1}{a_2}$ where a_1 equals the activity of the ion in the more concentrated solution.

TABLE I

Sols made in .001M KCl. Calculated EMF (.005M KCl − .001M KCl) = 39.87 mv.

Solution measured	Volume	Sparking time per liter	Observed potential	Gold content per liter
.001M KCl	.....	.....	40 mv.	.....
Sol No. 1	250 cc.	4 hours	43 mv.	264 mgms.
.001M KCl	.....	.....	40 mv.	.....
Sol No. 2	250 cc.	8 hours	47 mv.	612 mgms.
Sol No. 3	100 cc.	20 hours	56 mv.	872 mgms.
.001M KCl	.....	.....	40 mv.	.....
Sol No. 4	100 cc.	30 hours	58 mv.	764 mgms.
.001M KCl	.....	.....	40 mv.	.....
Sol No. 5	100 cc.	40 hours	63 mv.	628 mgms.
.001M KCl	.....	.....	40 mv.	.....
Sol No. 14	100 cc.	40 hours	66 mv.	560 mgms.
.001M KCl	.....	.....	40 mv.	.....
*Sol No. 13	100 cc.	30 hours	67 mv.	480 mgms.
.001M KCl	.....	.....	40 mv.	.....
Sol No. 7	100 cc.	60 hours	81 mv.	540 mgms.

TABLE II

Sols made in .002M KCl. Calculate EMF (.005M KCl − .002M KCl) = 22.92 mv.

Solution measured	Volume	Sparking time per liter	Observed potential	Gold content per liter
.002M KCl	.....	.....	23 mv.	.....
‡Sol No. 8	500 cc.	8 hours	28 mv.	696 mgms.
.002M KCl	.....	.....	23 mv.	.....
Sol No. 20	200 cc.	.....	32 mv.	860 mgms.
.002M KCl	.....	.....?.....	23 mv.	.....
Sol No. 9	100 cc.	20 hours	36 mv.	1032 mgms.
Sol No. 10	100 cc.	30 hours	43 mv.	628 mgms.
.002M KCl	.....	.....	23 mv.	.....
Sol No. 11	100 cc.	40 hours	49 mv.	540 mgms.
.002M KCl	.....	.....	23 mv.	.....
Sol No. 12	100 cc.	50 hours	56 mv.	616 mgms.

It was then decided to make sols in concentrations of KCl on either side of .001 M to observe the effect of change in concentra-

* Sol No. 13 stood for one week before being measured.

‡ Sols Nos. 8 and 15 were made by sparking 250 cc. portions of the KCl solution for 120 minutes each and combining the resulting sols.

tion on the character of the sol. Experiments which will be described later† indicated that .0003 M and .002 M were satisfactory concentrations. Therefore a series of sols were made in each of these. The results are given in Tables II and III. Tables I, II, and III are shown graphically in Figure I.

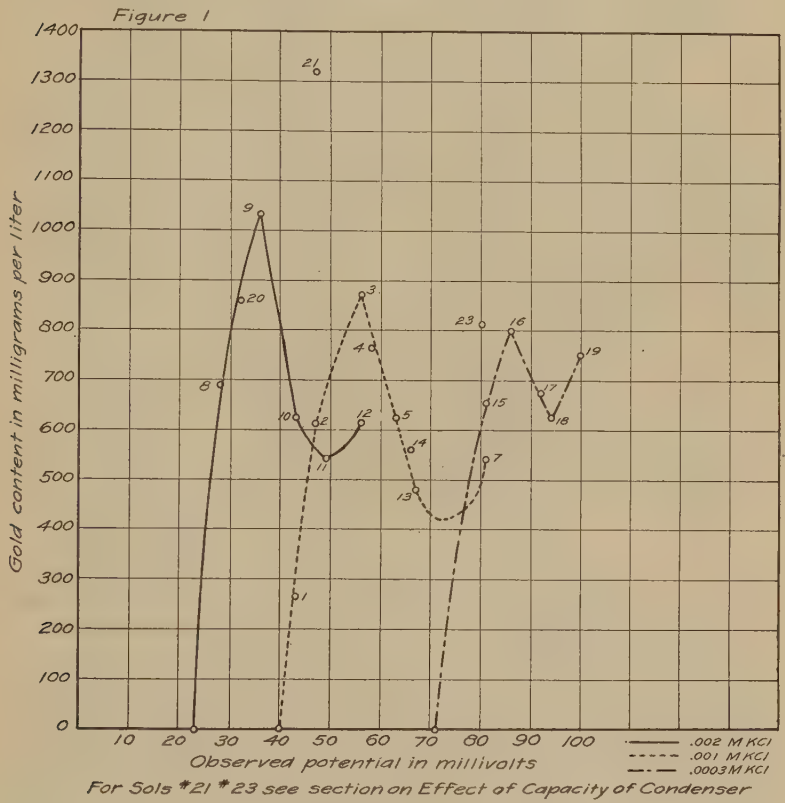


TABLE III

Sols made in .0003M KCl. Calculated EMF (.005M KCl − .0003 KCl) = 70.97 mv.

Solution measured	Volume	Sparking time per liter	Observed potential	Gold content per liter
.0003M KCl	.....	.....	71 mv.	.....
.0003M KCl	.....	.....	71 mv.	.....
‡Sol No. 15	500 cc.	8 hours	81 mv.	656 mgms.
.0003M KCl	.....	.....	71 mv.	.....

† See section on Effect of Original Concentration of Electrolyte.
‡ See footnote‡ page 12.

Solution measured	Volume	Sparking time per liter	Observed potential	Gold content per liter
Sol No. 16	100 cc.	20 hours	86 mv.	800 mgms.
.0003M KCl	.....	.....	71 mv.	.....
Sol No. 17	100 cc.	30 hours	92 mv.	676 mgms.
.0003M KCl	.....	.....	71 mv.	.....
Sol No. 18	100 cc.	40 hours	94 mv.	624 mgms.
.0003M KCl	.....	.....	71 mv.	.....
Sol No. 19	100 cc.	60 hours	100 mv.	756 mgms.

Effect of Original Concentration of Electrolyte

In order to determine qualitatively the effect of the original concentration of electrolyte upon the character of the sols made with the condensed spark the following series of experiments were made. 100 cc. of varying concentrations of KCl were placed in steamed and dried non-sol bottles; the electrodes were inserted into the bottle and a spark was run for one or two minutes. The results are recorded in Tables IV and V.

TABLE IV

Sparking time: 2 minutes

Sol No.	Conc. KCl	Color	Change
24	.00010 M	pale red	none
25	.00025 M	" "	"
26	.00050 M	" "	"
27	.001 M	bright red	"
28	.002 M	" "	"
29	.003 M	dark red	red in 1 hour
30	.004 M	bluish red	red in 12 hours
31	.005 M	blue	ppt'd in 2 weeks

In every case the sol was blue in color for the first few seconds of sparking, but changed more or less rapidly to red. When observed fifteen minutes after making, the series presented an even gradation in color from pale red through bright red to dark blue. It is this color which is recorded in the third column of Tables IV and V. The most marked color difference was between sols Nos. 29 and 30. Judging from color and permanence No. 27 was the best concentration of KCl to use, which agrees with the results of previous investigators on direct current sols.[7] On standing all sols either changed to red or precipitated, the blue color indicating an unstable condition.

In this series* also, although the color in each case was not as deep as in the preceding series, the same color gradations were observed. The most marked difference was between sols Nos. 39 and 40. It is to be noted that in .004 M KCl sparking for one

* See Table V.

minute did not produce a stable sol, while sparking for two minutes did.

TABLE V

Sol No.	Sparking time: 1 minute Conc. KCl	Color	Change
*32	0.0	no sol	....
33	.0001 M	pale red	none
34	.00025 M	" "	"
35	.0005 M	" "	"
36	.001 M	bright red	"
37	.002 M	" "	"
38	.003 M	dark red	"
39	.00325 M	" "	"
40	.0035 M	bluish red	red in 2 hours
41	.00375 M	" "	red in 12 hours
42	.004 M	blue	ppt'd in 3 weeks
43	.005 M	blue	ppt'd in 2 weeks
44	.01 M	no sol	.....

Effect of Centrifuging at 1200 Times Gravity on the Activity of the Electrolyte and Gold Content of the Sol

In order to determine the effect of centrifuging at 1200 times gravity on the activity of the electrolyte in the sol, in cases where the volume of the sol permitted, the potential was measured before and after centrifuging for 15 minutes at 1200 times gravity. The results are recorded in Table VI.

TABLE VI

Sol No.	Potential against .005 M KCl Before centrifuging	After centrifuging
1	43 mv.	43 mv.
8	28 mv.	28 mv.

To determine the effect of centrifuging at 1200 times gravity on the gold content of the sol the following experiment was carried out. Six 20cc. portions of the same sol were centrifuged for varying lengths of time at 1200 times gravity. Ten cc. were then pipetted out and analyzed for gold. The results are given in Table VII.

TABLE VII

Sol No. 6. 250 cc. .003 M KCl Sparking time: 4 hours per liter.

Time of centrifuging	Gold content per 10 cc.
½ hour	.0037 grams
1 "	.0037 grams

* Sol No. 32 was made in pure water having a specific conductivity of 1×10^{-6} mhos.

Time of centrifuging	Gold content per 10 cc.
2 hours	.0037 grams
3 "	.0033 grams
4 "	.0040 grams
5 "	.0038 grams

It will be noted that the gold content remained constant within the limits of precision of the analysis.

Effect of Freezing Upon the Activity of the Electrolyte in the Sol

To determine the effect of freezing on the activity of the electrolyte in the sol, when the volume permitted, the potential was measured and then the sol was placed in a non-sol bottle and frozen in an ice-box at about $-5°C$ until upon melting it gave a perfectly clear, colorless solution, the gold being completely precipitated. The potential of this solution was then measured. The results are given in Table VIII.

TABLE VIII

Sol No.	Conc. KCl	Potential against .005 M KCl	
		Before freezing	After freezing
1	.001 M	43 mv.	43 mv.
2	.001 M	47 mv.	45 mv.
20	.002 M	32 mv.	32 mv.
21	.001 M	47 mv.	46 mv.
23	.0003 M	80 mv.	77 mv.

This indicates that there is no considerable release of chloride ion when the sol is precipitated by freezing, i.e., the complex is stable. These results differ from those of Beaver and Shear for sols made with the direct current arc. They both observed a decided recovery of chloride ion after freezing. As stated in the introduction this is probably due to the electrolysis of the solution when making sols with the direct current arc.

Effect of Capacity of Condenser

Sols Nos. 21 and 23 were made with a condenser of approximately 8.8 microfarad capacity across the spark gap in place of the 1 microfarad condenser used in making the other sols. This resulted in a much more vigorous spark. The data on these sols are given in Table IX.

TABLE IX

Sol No.	Conc. KCl	Sparking time per liter	Observed potential	Gold content per liter
21	.001 M	6 hours	47 mv.	1320 mgms.
23	.0003 M	5 hours	80 mv.	816 mgms.

It will be noted from Figure 1 that this change in the capacity of the condenser affects the character of the sol in considerable degree. Sol No. 21 should be on the .001 M curve and No. 23 should be on the .0003 M curve. This effect was not studied further, but is in agreement with the results obtained by Svedberg.[12]

Reproducibility of Sols

Sols Nos. 13 and 14 were made and measured two months after the completion of sols Nos. 1 to 7, and were made in a freshly prepared solution of .001 M KCl, using different gold electrodes. They were also measured with different AgCl electrodes. Yet it will be observed that the values for these sols fall on the curve already obtained for sols Nos. 1 to 7, indicating the reproducibility of sols made and measured in this manner.

The same statement applies to sol No. 20 which was made and measured two months after the completion of sols Nos. 8 to 12. Shear's results on sols made with the direct current arc indicate no similar degree of reproducibility. This is probably due to the complications introduced by the electrolysis of the solution.

Factors Affecting the Composition of Sols

From the experiments conducted the author concluded that the composition of the sols made in this manner is not affected by:

(1) Variations in the temperature of the solution between 0°−25°C during sparking.
(2) Rate of stirring during sparking.
(3) Amount of electrode surface exposed.
(4) Variations in time of centrifuging from 30 minutes to 6 hours at 1200 times gravity.

The composition is affected by:

(1) Original concentration of electrolyte.
(2) Time of sparking.
(3) Character of the spark.

Work by previous investigators[7] in this laboratory has, of course, shown that the character of the sol is also affected by the nature of the electrolyte used.

VII. Discussion

To obtain some idea of the relationship between chloride ion activity lost and colloidal gold present, the figures in Tables I, II, and III were used to calculate the activity of chloride ion in the solution before and after sparking. Since there were no detectable amounts of electrolytic products formed, it is reasonable to assume that the chloride ion consumed was used in the formation of a complex with the gold particles, as stated by Beans and Eastlack and all subsequent workers in this laboratory.

To obtain these chloride ion activities the observed potentials were substituted in the Nernst equation: $E = .059 \log_{10} \frac{a_1}{a_2}$ in which a_1 was known. This equation was then solved for a_2 which was the desired activity. The results are given in Tables X, XI, and XII.

TABLE X

Sols made in .001 M KCl

Sol No.	Chloride ion activity m. p. l.	Loss in chloride ion activity m. p. l.	Gold content mols per liter
.001 M KCl	.00098	0	0
1	.00088	.00010	.00134
2	.00076	.00022	.00310
3	.00053	.00045	.00442
4	.00049	.00049	.00388
5	.00040	.00058	.00319
14	.00036	.00062	.00284
13	.00035	.00063	.00244
7	.00020	.00078	.00274

TABLE XI

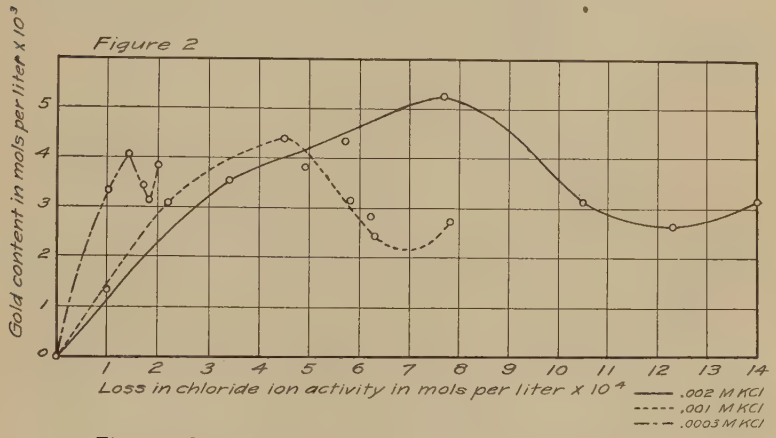
Sols made in .002 M KCl

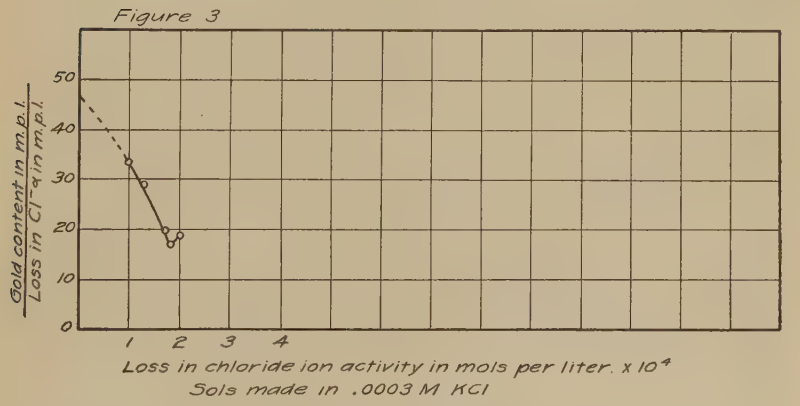
Sol No.	Chloride ion activity m. p. l.	Loss in chloride ion activity m. p. l.	Gold content mols per liter
.002 M KCl	.00193	0	0
8	.00159	.00034	.00354
20	.00136	.00057	.00436
9	.00116	.00077	.00524
10	.00088	.00105	.00319
11	.00070	.00123	.00274
12	.00053	.00140	.00313

TABLE XII

Sol No.	Sols made in .0003 M KCl Chloride ion activity m. p. l.	Loss in chloride ion activity m. p. l.	Gold content mols per liter
.0003 M KCl	.00030	0	0
15	.00020	.00010	.00333
16	.00016	.00014	.00406
17	.00013	.00017	.00343
18	.00012	.00018	.00317
19	.00010	.00020	.00384

These results are given graphically in Figure 2.





Note.—It should be noticed that since Nernst's equation is a logarithmic function of activity, at small values of a_2 any given change in a_2 produces a much larger change in the potential than an equal change does at larger values of a_2. For example when a_2 drops from .00098 to .00088, it corresponds to a change in

potential of 3 millivolts, while the same change from .00030 to .00020 corresponds to a change in potential of 10 millivolts. Therefore, although it is possible, we find difficulty in obtaining an accuracy of 1 millivolt in potential readings for these small values of a_2. This, however, does not change the precision of our final results.

The experimental results obtained may well be considered under three main headings: (1) Growth of colloidal particles in the sol. (2) Existence of a complex. (3) Nature of the complex.

(1) Growth of Colloidal Particles in the Sol

It will be noticed from Figures 1 and 2 that as sparking is continued the gold content of the sol rises to a maximum, then decreases to a minimum and again starts to rise. It appears to the author that this phenomenon is the result of a mechanical building up of colloidal particles until they are too large to resist centrifuging for 15 minutes at 1200 times gravity. That is, when the conditions are right for the formation of colloidal particles they will form and then grow in a purely physical manner. Of course the centrifuging is done primarily to get rid of suspended matter not truly colloidal in nature and the speed and time of centrifuging were arbitrarily chosen because they gave a sol of constant composition. Other speeds and times might be chosen, in which case we might expect differing but similar results, i.e., the new curves obtained would be similar to those in Figures 1 and 2 but would have different slopes.

Let us then assume that there may be present in the sol colloidal particles which are composed of one or more chloride ions to which may be attached any number of gold atoms from 1 up to a maximum which is determined by the size of the particle which will just resist our standard centrifuging. With this assumption in mind let us follow the curves obtained.

Sols Made in .002 M KCl

As sparking is continued in this solution the gold, from the condensing vapor from the electrodes, builds up on the chloride ions present and the gold content of the sol rises until a maximum is reached. The gold content of the sol at this point is propor-

tional to the number of chloride ions originally present, since the greater this original concentration, the larger will be the number of ions attaining a maximum gold content simultaneously. From this maximum the number of gold atoms per chloride ion ranges down to 1. Now if we spark longer the next gold particle attached to the chloride ion is sufficient to throw down the entire mass under the conditions of the experiment. Therefore the gold content of the sol decreases instead of remaining a constant. For if we consider two particles, one containing 30 gold atoms and the other 45 gold atoms, and add one gold atom to each, we may imagine that the one containing 31 gold atoms remains in the sol while the one with 46 is thrown out. So instead of increasing the gold content by 2 atoms we have decreased it by 44. In other words, gold is being thrown out of the sol faster than it is being put in.

This process continues until the number of these large particles is so decreased that the gold is being built up on the small particles faster than it is being removed by the settling out of the large particles. At this point, therefore, we have a minimum in the gold content curve and from there on it rises. It is to be expected that further sparking would produce a series of these maxima and minima, the curve taking the form of a damped oscillation.

Sols Made in .001 M KCl

On comparing the data on sols made in .001 M KCl with those from sols made in .002 M KCl we see that the gold content curve rises more rapidly to a maximum in the former. This is due to the fact that since there are fewer chloride ions present they must be built up to their maximum gold content faster than in the case of .002 M KCl. Also the maximum gold content of the whole sol is lower than for .002 M KCl because there are not as many chloride ions present to attain their maximum gold content simultaneously. Further we have the gold content curve dropping away more sharply from the maximum in the .001 M KCl sols.

Sols Made in .0003 M KCl

Similar reasoning may be applied to the results of sols made in this concentration of electrolyte. In this explanation it is

assumed that the maximum amount of gold on any one chloride ion is the same no matter what the original concentration in which the sol was made. It is further assumed that when the particle settles out the chloride ion is not released, for we get a continuous loss of chloride ion with continued sparking.

This explanation agrees with Briggs' for growth of particles in sols made with the direct current arc. He, however, did not obtain a minimum in the gold content curve.

Ratio Between Gold and Chloride Ion

The establishment of a ratio between chloride ion consumed and colloidal gold formed is complicated by the fact that the loss of chloride ion observed is due not only to the gold present in colloidal form, but also to that which has settled out either during the formation of the sol or during its centrifuging. This sludge consists of both particles of pure gold and colloidal particles which have grown too large.

The separation of this sludge into colloidal and non-colloidal gold is at present beyond the limits of analytical chemistry, but efforts are being made in this laboratory to find some means of avoiding a mixture of the two and thus gain a more precise idea of the above mentioned ratio. This determination is, of course, further complicated by the fact that the number of gold particles per chloride ion in the sol varies over a considerable range. Our results present only a statistical average.

However an approximation to the maximum number of gold atoms per chloride ion may be obtained in the following manner. If we obtain the ratio $\frac{\text{gold}}{\text{chloride ion}}$ in the first few minutes of sparking before any sludge has formed the first difficulty may in some degree be avoided. Again it will be noticed that the gold content curve for .0003 M KCl sols rises most steeply to its maximum, showing that the ions attain their maximum gold content most speedily. Therefore in Figure 3 we have plotted $\frac{\text{gold content}}{\text{loss in chloride ion}}$ against loss in chloride ion for sols made in .0003 M KCl. Extrapolation to zero loss in chloride ion gives 47 as the number of gold atoms per chloride ion.

(2) Existence of a Complex

Previous investigators in this laboratory have shown that Bredig gold sols cannot be prepared in pure water, but that a small concentration of electrolyte is essential to their formation. Further this electrolyte must furnish an anion which is capable of combining chemically with gold, since sols were not obtainable in water containing only NO_3^- or $SO_4^=$ anions. Shear showed that in the formation of a sol there was a distinct loss in chloride ion which could not wholly be accounted for by electrolysis. The author has shown that even when electrolysis is absent there is still a loss in chloride ion and this loss is proportional to the amount of colloidal gold produced. The centrifuging and freezing experiments indicate that this chloride ion is tied up in a more or less stable way and is not released when the sol is precipitated by mechanical means. For we observe no considerable recovery of chloride ion after centrifuging or freezing the sol.

All of which establishes conclusively the existence of a gold-chloride ion complex as originally stated by Beans and Eastlack.

(3) Nature of the Complex

The evidence summarized in the preceding section together with the fact that these sols migrate to the anode when a current is passed through them; and give no test for ionic gold with alkaline hydrogen peroxide, leads to the conclusion that the colloidal particle is a complex of the type $(Au_xCl_y)^{y-}$ in which x varies from 1 to an undetermined maximum, and the ratio $\frac{x}{y}$ reaches a maximum value of 47, as nearly as can be determined from the experimental data. This type of complex is similar to the one pictured for chemically prepared hydrosols of the ferric oxide type.[3]

The above, however, offers no explanation of why the complex forms originally or why the sol is stable only in certain concentrations of electrolyte. J. A. Wilson[15] offers an explanation of the precipitation of gold sols by the addition of electrolytes, using the Donnan membrane equilibrium theory. In brief this pictures a colloidal gold particle prepared in KCl solution as consisting of a chloride ion joined to one or more gold atoms.

In the liquid layer immediately surrounding this particle there are K^+ ions held in the layer by the negative charge on the "complex" colloidal particle. These K^+ ions cannot diffuse away but K^+ ions and Cl^- ions may diffuse in from the bulk of the solution. Thus, in effect, we have surrounded the particle with a semi-permeable membrane. Now according to the Donnan theory, at equilibrium the total concentration of the ions in the surface layer will be greater than in the bulk of the solution. This difference in concentration causes a difference in potential between the particle and the bulk of the solution. It is this potential difference which prevents coagulation of the colloidal particles. This potential difference may be decreased by increasing the concentration of electrolyte in the bulk of the solution and when it passes a certain point, not necessarily zero, coagulation takes place.

This theory is not capable of experimental proof in the case of Bredig gold sols since we have no way of measuring or calculating the potential between the particle and the bulk of the solution. We cannot follow the changes of this potential as the sol is precipitated, so the process is still a matter for speculation. The author wishes to call attention to certain phenomena which may be of value in future work.

It will be noted from Tables IV and V that all sols when first made up were blue in color indicating an unstable condition. They changed more or less rapidly to red, which color apparently indicated a stable condition. We have therefore in a stable sol a condition of equilibrium between the colloidal particles and the electrolyte in solution. The speed with which this equilibrium point is reached is inversely proportional to the original concentration of electrolyte. If the original concentration of electrolyte is too great, this equilibrium point is never reached and the sol remains unstable, settling out on standing.

It will be noted further that in the case of .004 M KCl one minute of sparking did not produce a stable sol whereas two minutes did. This indicates that by sparking for two minutes the concentration of electrolyte was decreased enough to enable a stable equilibrium to be reached between particle and solution. One minute of sparking did not reduce it sufficiently. From this the author concludes that it would be possible to obtain sols in higher concentrations of KCl than .004 M if the sparking were

continued long enough. Miller obtained sols in .005 M KCl using the direct current arc.

The point of interest, therefore, is that at which the concentration of KCl present in contact with the colloidal particle is slightly less than .004 M. Below that concentration a condition of stable equilibrium may be attained; above it the sol is in an unstable state.

The author offers the following theory in explanation of these phenomena, not with the idea that it is necessarily the correct one, but with the hope that it may furnish a basis for criticism and further experimentation.

Let us assume then that the following changes occur in the formation of the colloidal particle:

$$xAu + yCl^- \underset{\text{red}}{\rightleftarrows} (Au_xCl_y)^{y-} + zCl^- \underset{\text{blue}}{\rightleftarrows} (Au_xCl_{y+z})^{(y+z)-}$$

That is, when x gold atoms are torn loose from the electrode, they may combine with yCl^- ions to give the complex $(Au_xCl_y)^{y-}$ which results in a stable sol. But this particle in turn may combine with more Cl^- ions to give the complex $(Au_xCl_{y+z})^{(y+z)-}$ which precipitates out, possibly as $Au_x \cdot KCl_{(y+z)}$. Briggs has shown that color does not depend on size of particles in the sol, so we must conclude that a change from red to blue indicates a chemical change.

This blue coloration is the one we always get in the first few minutes of sparking because the particle is formed in the presence of an excess of chloride ion. But as sparking is continued or the sol is allowed to stand there is a change from blue to red resulting in a stable particle. The presence of an excess of chloride ion forces the reaction completely to the right with the formation of the unstable particle, the result being that the sol precipitates upon standing. Again the addition of an excess of electrolyte to a stable sol forces the above reaction to the right with the same result. On the other hand too small an amount of chloride ion in the solution forces the reaction to the left and results in the precipitation of pure gold; this being the result which we observe when a spark is run in water having a specific conductivity of 1×10^{-6} mhos or less.

In the above discussion the author has omitted consideration of the effect of the positive ion since in his work this ion was

always the potassium ion. A study of the effect of varying the character of the positive ion is left for future work.

VIII. Summary

(1) Bredig gold sols have been made in which there are no detectable traces of chloride ion oxidation products.

(2) The activity of the chloride ion in these sols has been determined by means of potential measurements, using a silver chloride gauze electrode. These measurements have been made in concentrations of chloride ion as low as .0001 M with a precision of 1 millivolt and are reproducible.

(3) The activity of chloride ion in a KCl solution is lessened due to the formation of colloidal gold.

(4) The amount of colloidal gold formed is proportional to the loss in chloride ion activity.

(5) Centrifuging the sol for 15 minutes at 1200 times gravity does not decrease the chloride ion activity but does produce a sol of constant gold content.

(6) Precipitation of the sol by freezing produces no appreciable change in the chloride ion activity, indicating a stable colloidal complex.

(7) An explanation is offered for the growth of colloidal particles in the sol which agrees with previous explanations.

(8) Further proof is offered of the existence of a complex as stated by Beans and Eastlack.

(9) A theory of the nature of the complex is offered which explains satisfactorily the observed phenomena.

Bibliography

[1] Bredig—Inaug. Diss., Leipsig (1901).
[2] Graham—Chem. and Phys. Researches, p. 580 (1876).
[3] Thomas—J. Chem. Ed., *2*, 323 (1925).
[4a] Bancroft—B. A. Reports on Coll. Chem., II, 6 (1918).
[b] Holmes—Lab. Man. of Coll. Chem., p. 18 (1922).
[c] Zsigmondy-Spear—Chem. of Coll., p. 93 (1917).
[d] Ostwald-Fisher—Theor. and Appl. Coll. Chem., p. 33 (1917).
[e] Duclaux—Les Colloides, p. 17, 19, 20 (1920).
[5] Beans and Eastlack—J. A. C. S., *37*, 2667 (1915).
[6] Beaver—Diss. for Ph.D., Columbia (1921).
[7] Miller—Diss. for Ph.D., Columbia (1922).
[8] Briggs—Diss. for Ph.D., Columbia (1923).
[9] Davidson—Diss. for Ph.D., Columbia (1924).
[10] Shear—Diss. for Ph.D., Columbia (1925).
[11] MacInnes & Beattie—J. A. C. S., *42*, 1118 (1920).
[12] Svedberg—Colloid Chem.—A. C. S. Monograph Series, 1924, pp. 39, 40, 43, 58.
[13] Morgan—Elements of Phys. Chem., 5th Ed., p. 441 (1914).
[14] Lewis & Randall—Thermodynamics, p. 344 (1923).
[15] Wilson—J. A. C. S., *38*, 1982 (1916).

VITA

John Page Amsden was born in Attleboro, Massachusetts, on May 23, 1899. He attended the public schools of Concord, New Hampshire, graduating from the High School in 1916. He received the degree of A.B. from Dartmouth College in 1920. From 1920 to 1922 he was Instructor in Chemistry at Dartmouth. In 1922 he entered the Graduate School of Columbia University and received the degree of M.A. in 1923. In 1924–1925 he was again a student at Columbia University. In 1925 he was appointed Instructor in Chemistry at Dartmouth, which position he now holds. He is a member of the following honorary societies: Phi Beta Kappa, Gamma Alpha, Phi Lambda Upsilon, Sigma Xi, and Alpha Chi Sigma.

JUN-4'32